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AN INVESTIGATION OF THE EFFECT OF SURFACE IMPURITIES ON THE ADSORPTION KINETICS OF HYDROGEN CHEMISORBED ONTO IRON

M. R. SHANABARGER

Quantum Institute

University of California, Santa Barbara

Santa Barbara, California 93106

Submitted to: H. G. Nelson, Chief

Test Engineering and Analysis Branch
NASA-AMES Research Center
MS: 213-3
Moffett Field, California 94035

cc: NASA Scientific and Technical Information Facility
P.O. Box 8757
Baltimore/Washington International Airport
Maryland 21240

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1.0 INTRODUCTION

The goal of this program has been to develop an understanding of heterogeneous kinetic processes for those molecular species which produce gaseous hydrogen degradation of the mechanical properties of metallic structural materials. Although hydrogen degradation of metallic materials is believed to result from dissolved protonic hydrogen [1,2], the heterogeneous hydrogen interface transport processes often dominate the kinetics of degradation [3]. The initial step in the interface transport process is the dissociative chemisorption of the molecular species at the metal surface followed by hydrogen absorption into and transport through the bulk [4].

Modern advanced aerospace applications often require the use of structural materials in high pressure hydrogen environments at temperatures which range from low cryogenic temperatures to very high temperatures (1300 K and greater) [5]. Materials proposed for these applications, such as the titanium aluminides, beta-titanium alloys, iron-, nickel- and cobalt-based superalloys, and molybdenum-rhenium alloys need to possess a high degree of immunity from hydrogen induced degradation of mechanical properties. In addition, most of these materials require the use of ceramic protective coatings to inhibit high temperature oxidation [6,7]. Little is known about the interaction of hydrogen with many of these materials and the possible influence of hydrogen on the material's mechanical properties or the coating's protective performance [8]. It can be expected that the interaction of gaseous environmental hydrogen with these materials will be influenced by the gas phase-surface reaction process. The present study was established in 1988 to develop an understanding of the interaction of gaseous hydrogen with these materials and to evaluate hydrogen transport through them. This study supersedes, for the present, the work begun earlier under this agreement, which was to study the influence that surface impurities have in modifying the kinetics for hydrogen chemisorption on pure iron.

During the present program, the interaction of hydrogen with the surfaces of alpha-2 (Ti_3Al) titanium aluminide [9], gamma (TiAl) titanium aluminide [10], and beryllium [11] were studied. The interaction of low pressure hydrogen with gamma titanium aluminide and beryllium was found to be relatively weak. Weak in the sense that adsorption leads to a low surface concentration of dissociated hydrogen, i.e., the chemisorption process is reversible at room temperature (300 K) for gamma titanium aluminide and the sticking coefficient for chemisorption is extremely small for beryllium. Hydrogen was found to interact readily with alpha-2 titanium aluminide to form a stable surface hydride at 300 K. These results correlate well with other recent studies which show that the mechanical properties for alpha-2 titanium aluminide are readily degraded in hydrogen while gamma titanium aluminide exhibits less degradation and beryllium essentially no degradation [12]. The interaction of oxygen with the surface of several of these materials was studied[13]. More recently, preliminary hydrogen permeation studies were completed for two high temperature alloys, Incoloy 909 [14] and Mo-47.5Re (wt.%) [15], and this past year measurements were initiated for the alloy, Haynes 188 [16].

The remainder of this document presents a narrative summary of the research activities completed during the award period, January 1, 1993 to December 31, 1993.

2.0 SUMMARY OF RESEARCH ACTIVITIES

Work supported by this agreement has covered a spectrum of activities during the present award period. The focus of the technical activity was to complete a study of hydrogen and deuterium permeation in Haynes 188 alloy. Technical problems, to be discussed below, postponed this activity. A significant portion of time was spent on non-research activities in providing technical support to the National Aero-Space Plane (NASP) Program. In this capacity, a high sensitivity gas sampling system was designed and procured for the NASA-Ames Hydrogen Charging Apparatus. A considerable amount of time was spent, as well, in critically reviewing the existing database of randomly performed measurements of hydrogen absorption in the titanium aluminide alloy Ti-24Al-11Nb and establishing the most plausible parameters for hydrogen solubility in this alloy.

2.1 Permeation - Experimental

Initial measurements of H_2 permeation through Haynes 188 alloy were made. During these initial measurements, a failure occurred in the turbo molecular pumping system. The turbo molecular pump is the main vacuum pump on the permeation apparatus and without it further measurements were not possible.

The time required to complete repair of the turbo pump was quite lengthy, primarily because of the procedures required by NASA-Ames Research Center for the repair process. Because of the lengthy down time, it was decided to proceed with modifications to the Lepel rf generator used to inductively heat the permeation specimen to temperature. All repairs and modifications were completed by late September and reassembly of the permeation apparatus was begun. This has led to a seven month delay in the program.

Preliminary values for the hydrogen transport parameters in Haynes 188 from measurements prior to the indicated equipment problems were determined to be:

$$\Phi = 1.29 \times 10^{18} \exp(-61.5 \mathrm{kJmol}^{-1} / RT)\ H_2 / m - s - \sqrt{Pa}\ ,$$

$$D \approx 3.84 \times 10^{-6} \exp(-50.2 \mathrm{kJmol}^{-1} / RT)\ m^2 / s\text{, and}$$

$$C \approx 3.35 \times 10^{23} \exp(-11.3 \mathrm{kJmol}^{-1} / RT)\ H_2 / m^3 - \sqrt{Pa}\ .$$

These results were obtained with a cylindrical permeation specimen having a gauge section of 5.08×10^{-4} m. Here Φ is the hydrogen permeability, D the protonic hydrogen lattice diffusivity, and C, the hydrogen solubility. The result for Φ is reliable, in the sense that it was obtained from a series of different measurements completed over a period of time. These measurements covered the temperature range of 350 C to 840 C. The values for D and C are less accurate, since they were obtained from a limited set of measurements. Finally, the permeation flux was observed at two temperatures (650 and 760 C) to be proportional to $\sqrt{p_{H_2}}$ over the pressure range of 1.33 kPa to 114 kPa.

2.2 Permeation - Modeling

A computer program was written to simulate permeation through a cylinder. The program was used to confirm the value of the constant used in the formula to obtain a value for the diffusivity from the break-through time, t_{bt}. A value for this constant was estimated earlier from experimental data for H_2 permeation through INCOLOY 909. The simulation accurately reproduced the experimentally derived values. Specifically, for a cylindrical geometry, the break-through time is given by:

$$t_{bt} = \frac{r_i^2 - r_o^2 + (r_i^2 + r_o^2)\ln(r_o / r_i)}{13.6 \cdot D \cdot \ln(r_o / r_i)} ,$$

where, t_{bt} is the measured break-time, r_i is the permeation specimen's inner radius, r_o is the outer radius, and D, the diffusivity of the specimen. The relationship between the break-through time and the more traditional lag-time is as follows:

$$t_{lag}/t_{bt} = 3.5.$$

2.3 Surface Characterization

There were no significant research activities in the surface characterization area during the present award period.

2.4 Other Activities

A. *Meetings Attended (present award period)*

1. Twenty-ninth Annual Symposium of the AVS/NM and the 18th DOE Surface Studies Conference, April 27-30, 1993, Santa Fe, New Mexico, presenter and participant.

2. 1993 Gordon Research Conference on Hydrogen-Metal Systems, July 18-23, 1993, Tilton, New Hampshire, presenter and participant.

3. 1993 TMS Fall Meeting, October 17-21, 1993, Pittsburgh, Pennsylvania, presenter and participant.

B. *Presentations Made (present award period)*

1. Hydrogen Materials Testing for Generic Hypersonic Engines and a Survey of National Facilities, H.G. Nelson and M.R. Shanabarger (presentation by H.G. Nelson), contributed presentation, Workshop on Hydrogen Corrosion in Nuclear Thermal Propulsion Reactors, January 9, 1993, Albuquerque, New Mexico.

2. Coverage Dependence of the Sticking Coefficients for CO, O_2, and H_2S Adsorption onto Evaporated Fe Films, contributed presentation, 29th Annual Symposium of the AVS/NM and the 18th DOE Surface Studies Conference, Santa Fe, New Mexico, April 27-30, 1993.

3. A Specific Model for Hydrogen Transport through Iron Membranes including Surface Reactions, M. R. Shanabarger, contributed presentation, 1993 Gordon Research Conference on Hydrogen-Metal Systems, Tilton, New Hampshire, July 18-23, 1993.

4. Parameters for Deuterium Transport in Mo-47.5Re, M. R. Shanabarger, contributed presentation, 1993 TMS Fall Meeting, Pittsburgh, Pennsylvania, October 17-21, 1993.

C. *Publications*

The following have been published, submitted for publication, or were in preparation for publication during the present award period:

1. Hydrogen Barrier Coatings for High Temperature NASP Materials: Problems and Challenges, A.S. Khan and M.R. Shanabarger, in Summary Proceedings of the 4th Workshop on Hydrogen Material Interactions, H.G. Nelson, ed., NASP Workshop Publication 1013 (Langley Research Center, February, 1993) p. 267-275.

2. Summary Report on an Investigation of Hydrogen Adsorption on Beryllium, M.R. Shanabarger, in Summary Proceedings of the 4th Workshop on Hydrogen Material Interactions, H.G. Nelson, ed., NASP Workshop Publication 1013 (Langley Research Center, February, 1993) p. 307-313.

3. Gas Phase Hydrogen Permeation in a Ni-Fe-Co Superalloy, Mickey R. Shanabarger, *Scripta Metallurgica et Materialia*, 28(1993)1143-1148.

4. Hydrogen Materials Testing for Generic Hypersonic Engines and a Survey of National Facilities, with H.G. Nelson, submitted for publication in the *Proceedings of the Workshop on Hydrogen Corrosion in Nuclear Thermal Propulsion Reactors*, Albuquerque, New Mexico, January 9, 1993.

5. Diffusivity and Solubility of Deuterium in a Mo-Re Alloy, Mickey R. Shanabarger, to be published in *Scripta Metallurgica et Materialia* (March 15, 1994, vol. 30-6).

6. A Study of the Interaction of Hydrogen with the Surface of Titanium-Aluminum Intermetallic Alloys, Mickey R. Shanabarger, to be published in *Zeitschrift für Physikalische Chemie*.

7. ESR Studies of Dilute Local Moment Alloys, Harris Flam, Mickey R. Shanabarger, and S. Schultz, in preparation.

D. *Technical Reports*

1. An Investigation of the Effect of Surface Impurities on the Adsorption Kinetics of Hydrogen Chemisorbed onto Iron, M.R. Shanabarger, Annual Status Report, NASA-Ames Cooperative Agreement No. NCC-2-63, January 1 to December 31, 1992, submitted to Howard G. Nelson, NASA-Ames Research Center, February, 1993.

2. Quarterly Activity Report (January through March, 1993) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center, May 10, 1993.

3. Quarterly Activity Report (April through June, 1993) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center, August 11, 1993.

4. Hydrogen Solubility in Ti-24Al-11Nb (at.%), submitted to H.G. Nelson of NASA-Ames Research Center, October 1, 1993.

5. Quarterly Activity Report (July through September, 1993) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center, November 2, 1993.

5. Quarterly Activity Report (October through December, 1993) for NASA Cooperative Agreement NCC-2-63, submitted to Howard Nelson of NASA-Ames Research Center, January 19, 1994.

3.0 REFERENCES

1. H. G. Nelson, in *Treatise on Materials Science and Technology, Embrittlement of Engineering Alloys*, C. L.Briant and S. K. Banerji, eds. (Academic Press, New York, 1983), vol. 25, p. 344.

2. M.R. Shanabarger, in *Second Workshop on Hydrogen Effects on Materials in Propulsion Systems*, B.N. Bhat, D.L. Dreshfield, and E.J. Vesely, Jr., eds., NASA Conference Publication 3182(1992), p.12.

3. H. G. Nelson, D. P. Williams, and A. S. Tetelman, *Metall. Trans.* 2(1971)953.

4. *Chemisorption of Gases on Metals*, F.C. Tompkins (Academic Press, New York, 1978).

5. Advanced Materials to Fly High in NASP, T. M. F. Ronald, *Advanced Materials and Processes* 135(May, 1989)29.

6. *Oxidation of High-Temperature Intermetallics*, T. Grobstein and J. Doychak, eds. (The Minerals, Metals & Materials Society, Warrendale, 1988).

7. M.R. Shanabarger and A. Khan, in *Proceedings of the Eighth National Aero-Space Plane Technology Symposium* (NASA Langley Research Center, Langley, Virginia, 1990), Volume IV-Materials, p.107.

8. *Summary Proceedings of the Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1001, H.G. Nelson and M.R. Shanabarger, eds., (NASP Joint Program Office, Wright-Patterson AFB, Ohio,1987).

9. M.R. Shanabarger, in *Hydrogen Effects on Material Behavior*, N.R. Moody and A.W. Thompson, eds. (The Minerals, Metals & Materials Society, Warrendale, 1990), p.507.

10. M.R. Shanabarger, in *Summary Proceedings of the Third Workshop on Hydrogen-Material Interactions*, NASP Workshop Publication 1007, H.G. Nelson, ed. (NASP Joint Program Office, Wright-Patterson AFB, Ohio, 1990) p.205.

11. An Investigation of Hydrogen Adsorption on Beryllium, M.R. Shanabarger, to be published in the *Proceedings of the Fourth NASP Workshop: Hydrogen-Material Interactions*, Scottsdale, Arizona, 1990.

12. See articles in *Proceedings of the Fourth NASP Workshop: Hydrogen-Material Interactions*, Scottsdale, Arizona, 1990, to be published.

13. M.R. Shanabarger, *Materials Science and Engineering*, A153(1992)608.

14. Incoloy is a trademark of Inco Alloys International, Inc.

15. Hydrogen Permeation in INCO 909 and Mo-47.5Re: Preliminary Results, M.R. Shanabarger, to be published in the *Proceedings of the Fifth Workshop on Hydrogen-Material Interactions*, Scottsdale, Arizona, 1992.

16. Haynes 188 is a trademark of Haynes International, Inc.